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NO_x Storage and Reduction Over Copper-based Catalysts.

Part 3: Simultaneous NO_x and soot removal.

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Graphical Abstract



Highlights

- NO_x removal by NSR and soot combustion can be simultaneously carried out at 400°C
- The NSR process has a positive impact on the catalytic combustion of soot
- The effect of soot combustion on NO_x removal depends on the ceria dopant
- The effect is negative for CuO/Ce_{0.8}La_{0.2}O₈ (basic dopant) due to CO₂ chemisorption
- The effect is positive for CuO/Ce_{0.8}Zr_{0.2}O₈ (acidic dopant) due to NO_x reduction by soot

Abstract

5% copper catalysts with Ce_{0.8}M_{0.2}O₈ supports (M = Zr, La, Ce, Pr or Nd) were studied for the simultaneous combustion of soot and removal of NO_x by the NSR method. The simultaneous chemisorption of NO_x and combustion of soot could be carried out above 375°C, and nitrates were formed upon NO_x chemisorption above this temperature. The nature of the M dopant played an important role in the chemisorption of NO_x and in the catalysed soot-NO_x reaction. As a general trend, the presence of soot had a negative impact on NO_x removal by catalysts with very basic supports but had no effect or a positive influence if the support is not very basic. The combustion of soot has a very negative impact for NO_x chemisorption on the catalyst with the most basic dopant (CuO/Ce_{0.8}La_{0.2}O₈), because the CO₂ formed in the reaction of soot combustion competes with NO_x for adsorption sites. On the other hand, soot combustion does not affect NO_x chemisorption on the catalyst with the most acidic dopant (CuO/Ce_{0.8}Zr_{0.2}O₈), and the removal of NO_x increases in this case because the reduction of NO_x by soot contributes to NO_x removal. The simultaneous reduction of NO_x to N₂ and soot combustion can be carried out under NSR conditions at 400°C over the 5%Cu/Ce_{0.8}Pr_{0.2}O₈ catalyst and with H₂ micropulses, and the NSR process has a positive impact on the catalytic combustion of soot.

Keywords: NSR; deNO_x; soot; copper catalyst; Ceria; DRIFTS; Operando.

1.- Introduction

The main pollutants emitted by Diesel engines are nitrogen oxides and soot [1-6]. In these engines, the air-fuel mixture is compressed and this leads to the reaction between N_2 and O_2 yielding NO. Another pathway to NO formation is the oxidation of nitrogen heteroatoms present in fuel, but the former formation pathway is of greater significance in this type of combustion. As soon as the exhaust gas is released at the exhaust manifold, NO slowly reacts with O_2 forming NO_2 , and this NO + NO_2 mixture is generically referred to as NO_x because the NO/ NO_2 ratio depends on the O_2 and NO_x partial pressures, total pressure, temperature, contact time and presence of catalysts. The compression of the air-fuel ratio also produces heterogeneities in the composition of the combustion mixture, and the deficit of O_2 in particular spots leads to the partial pyrolysis of some hydrocarbons instead of total oxidation. Once the mixture of gases is released to the exhaust system, the pressure drops and gas cools, and the partially unburned hydrocarbons condense forming soot nanoparticles. In addition, soot also contains metals coming from lubricant oils and from the engine itself, adsorbed hydrocarbons and sulfur compounds.

There are different strategies for NO_x and soot removal from diesel engine exhausts [4-7]. The NSR process (NO_x Storage and Reduction) is one of the technologies for NO_x abatement, where a storage material is used to chemisorb NO_x and a reductant is periodically fed, which, in the presence of a catalyst, reduces the chemisorbed species to N_2 . The most widely studied NSR catalyst consists of Pt supported on a barium compound, where barium chemisorbs NO_x and Pt accelerates the oxidation of NO to NO_2 and catalyzes the reduction of the chemisorbed NO_x species. On the other hand, Diesel Particulate Filters (DPF) are employed to avoid soot release, and the soot collected on the

filters must be periodically removed by combustion [1-3]. Catalysts are also used to accelerate soot combustion, and Pt is one of the most active for this purpose.

Combined systems for the simultaneous removal of soot and NO_x have also been investigated [8] as this approach would be much simpler than conventional dual-bed configurations (deNO_x + deSoot). Perovskite [9-13], spinel [14,15], Ce-Zr [16] and Fe-K [17] mixed oxide catalysts have been studied, among others, for the simultaneous removal of NO_x and soot. In these studies, NO_x were reduced by soot in the presence of a catalyst without the addition of gaseous reductant. However, despite demonstrating that soot-NO_x reaction contributed to NO_x reduction, the NO_x conversion levels were low and additional NO_x removal strategies are required. Pisarello et al. [18] also explored this concept and studied the catalytic combustion of soot and the simultaneous reduction of NO_x by soot using Co-Ba catalysts with high NO_x storage capacity in order to enhance NO_x removal. They concluded that the chemisorption of NO_x on the catalysts partially inhibits the combustion of soot due to the formation of stable nitrates.

The combination of the NSR technology for NO_x removal with the simultaneous combustion of soot over the same NSR catalyst seems to be a more promising option for the abatement of both pollutants in a single catalytic bed, and this technology is usually referred to as DPNR (Diesel Particulate NO_x Reduction). Conventional Pt-Ba/Al₂O₃ NSR catalysts have been studied for the NO_x storage and reduction with H₂ and for the simultaneous combustion of soot, and it has been reported that the NO_x storage properties are hindered by the presence of soot [19-21].

In order to lower the cost of the NSR and soot combustion catalysts, noble metal-free formulations are also being investigated, and the goal of the current study is to evaluate the potential employment of noble metal-free copper/ceria-based formulations

for the simultaneous removal of NO_x and soot. On the one hand, ceria-based oxides are among the most efficient catalysts for accelerating soot combustion [16], and on the other hand, we have recently reported that ceria-supported copper formulations are suitable as NSR catalysts [22,23]. This article is the third of a series devoted to CuO/Ceria NSR catalysts. In the first article CeO₂+BaO supports were compared [22], and it was concluded that the NSR behavior of CuO/(CeO₂+BaO) catalysts with different proportion of CeO₂ and BaO (from 0 to 100% of each component) was similar. In the second article, CuO/Ce_{0.8}M_{0.2}O₈ (M = Zr, La, Ce, Pr or Nd) catalysts were compared, with the aim of improving the NSR performance of the CuO/CeO₂ catalyst [23]. It was concluded that the acid/basic character of the ceria dopants plays a key role. In the current article, CuO/Ce_{0.8}M_{0.2}O₈ catalysts are studied for simultaneous soot combustion and H₂-NSR deNO_x. The study was performed using *operando* DRIFTS in order to understand the reaction pathways and the potential synergies or interferences between the catalytic combustion of soot and the NO_x storage and reduction when both processes take place over the same catalyst.

2.- Experimental details

2.1. Materials

CuO/Ce_{0.8}M_{0.2}O₈ catalysts with M = Zr, La, Ce, Pr or Nd and 5 wt. % Cu have been used in this study. Details regarding their preparation and characterization were reported elsewhere [23,24].

The model soot used was a carbon black by Evonik-Degussa GmbH (Printex U), with $\sim 100 \text{ m}^2/\text{g}$, $< 0.1\%$ of ash, $\sim 5\%$ adsorbed hydrocarbons and with an overall composition, 92.2% C, 0.6% H, 0.2% N and 0.4% S.

Soot + $\text{CuO/Ce}_{0.8}\text{M}_{0.2}\text{O}_8$ mixtures were prepared in the so-called *loose contact* mode, which has been suggested to mimic the contact in a DPF filter [25]. The soot-catalyst mixtures were prepared with a spatula in a 1:20 weight ratio. This selected soot:catalyst ratio ensures that the solid bed remains stable during the combustion of soot, which is essential in order to attain spectra throughout the experiment.

2.2. Catalytic experiments

All catalytic tests were carried out under *operando* conditions using a Shimadzu Fourier Transform Infrared Spectrometer (IR Tracer-100) with a Harrick reaction cell coupled to a EcoSys-P mass spectrometer and a chemiluminescence NO_x analyzer (Thermo 42H). The sample holder of the DRIFT was 6.3 mm diameter and 3.3 mm deep with the full volume filled with sample. It should be noted that the infrared spectra obtained represent sample in the top *ca* 0.2 mm layer of the total solid [26].

The reaction cell was designed to allow the reaction gas mixture (50 ml/min; 850 ppm NO_x + 5% O₂ + N₂) to pass through the catalyst bed with the gas exit at the bottom. 105 mg of the soot-catalyst mixture were used in the soot combustion experiments, and several reference experiments were also performed with 100 mg of catalysts in the absence of soot.

It is worth mentioning that temperature control and monitoring within the DRIFTS cell is complex and it has been reported that the actual temperature of the catalyst

bed can be significantly lower than the set point with reported differences of around 50°C when the temperature is set at 400°C [27]. This must be kept in mind during interpretation and in particular, when relating data to information obtained using other devices (e.g reactors).

In all experiments, a background spectrum was recorded as described in each case, which was subsequently subtracted from the spectra recorded under reaction conditions. Therefore, the bands shown in the figures can be assigned to the formation or depletion of species on the catalysts.

Considering previous results [28], it was assumed that CO₂ was the main product of soot combustion and that this can be followed using the m/z 44 signal. The formation of CO was ruled out under current soot combustion catalytic experiments because the catalysts studied here are highly selective to CO₂ [28]. In addition, the maximum temperature reached was 500°C, and CO formation is favoured at higher temperatures.

Temperature programmed experiments were carried out by raising the temperature of the soot-catalyst mixtures until 150°C in a N₂ flow, and holding this constant for 15 min. A background spectrum was recorded of the catalyst at 150°C in N₂, and then, the inert gas was replaced by NO_x/O₂/N₂ and the temperature increased at 10°C/min until 500°C. In these experiments, 33 scans were averaged to obtain each spectrum, which were measured in the 4000-1000 cm⁻¹ range at 4 cm⁻¹ resolution.

Isothermal experiments were performed at 400°C with soot-CuO/Ce_{0.8}Pr_{0.2}O₈ mixtures with and without pulses of H₂. In these experiments, the temperature was increased from room temperature to 400°C under N₂, and then a background spectrum was recorded. The inert gas was then replaced by the NO_x/O₂/N₂ mixture, and considering this time as 0 min. In the isothermal experiments performed with H₂ pulses (NSR

experiments), 100 μl pulses of pure H_2 were fed with frequencies of 30 seconds starting as soon as the $\text{NO}_x/\text{O}_2/\text{N}_2$ gas mixture was delivered to the reaction cell. This frequency is in the range of realistic values proposed by Toyota [29-31].

In the isothermal experiments, the rapid-scan mode was used to follow these experiments with the DRIFT spectrometer, recording one spectrum per second as an average of 7 scans and the Rapid-scan Software (Shimadzu Corporation) used to handle the data. The spectra were obtained with a resolution of 8 cm^{-1} in the $4000\text{-}1000\text{ cm}^{-1}$ range. The gas composition was monitored in these experiments with the mass spectrometer, because in the experimental set-up used, the sampling frequency of the mass spectrometer was much faster to that of the chemiluminescence NO_x analyzer and was appropriate for fast screening. Comparison of the NO_x concentrations measured by chemiluminescence and mass spectrometry ($m/z\ 30$) confirmed that both techniques provide comparable results. The limitation of following the $m/z\ 30$ signal is that it is unable to distinguish NO and NO_2 , but rather provides values of total NO_x .

3.- Results and discussion

3.1. Temperature programmed NO_x storage experiments

Figure 1 shows results of the temperature programmed experiments performed with loose contact soot-catalyst mixtures (except where indicated). The $m/z\ 44$ signals corresponding to CO_2 are plotted in Figure 1a, and these signals can be used to evaluate the combustion of soot. It was confirmed experimentally that in the absence of catalysts, no conversion of soot took place in the range of temperatures of these experiments ($150\text{-}500^\circ\text{C}$). Temperature programmed experiments were also carried out with the catalysts

without soot for reference purposes, and the m/z 44 signal monitored with $\text{CuO/Ce}_{0.8}\text{Pr}_{0.2}\text{O}_8$ is plotted in Figure 1a as an example. It was observed that the release of CO_2 due to e.g. carbonate decomposition was negligible with regard to the amount of CO_2 emitted due to soot combustion, and it was therefore concluded that carbonate decomposition does not interfere in the monitoring of soot combustion while following the m/z 44 signal.

The onset temperature for CO_2 release in soot combustion experiments (Figure 1a) was 375°C for all catalysts, and most of them showed very similar behavior. This temperature was consistent with typical literature values for the model carbon black used in this study and for other ceria containing soot combustion catalysts [32, 33]. Total combustion of soot was not achieved under these conditions due to a limitation in the maximum temperature attainable in the DRIFTS cell (500°C). For this reason, the soot combustion capacity of the different catalysts are compared using results obtained in the isothermal experiments, where total soot combustion was achieved.

Figures 1b and 1c show the NO_x and NO_2 profiles, respectively, monitored using the chemiluminiscence NO_x analyzer, during temperature programmed soot combustion experiments. NO is the most abundant of the nitrogen oxides in the gas mixture fed to the reactor, in accordance with typical NO_x ratios found for real diesel exhausts. All catalysts accelerated NO oxidation to NO_2 above 300°C , and the NO_2 percentage increased until approximately 425°C where the thermodynamic equilibrium was attained (Figure 1c). The NO oxidation capacities of all catalysts studied were similar, and therefore, any relationship between NO oxidation activity and the different NO_x chemisorption behavior observed in Figure 1b can be ruled out.

Figure 1b shows NO_x curves as crossing the reference NO_x profile obtained using the empty reactor. At low temperatures, the NO_x levels obtained with the soot-catalyst mixtures were below the reference level, because NO_x was removed from the gas mixture, while above a threshold temperature, all catalysts released NO_x and their concentrations were above the reference level. The NO_x profiles obtained in reference temperature-programmed experiments performed with the catalysts alone (Ce_{0.8}Pr_{0.2}O₈ is included in Figure 1b as an example) were quite similar to those obtained with soot-catalyst mixtures. Therefore, in these experiments, the removal and release of NO_x observed with soot-catalyst mixtures can be mainly attributed to NO_x chemisorption on the catalysts and to further decomposition of the stored species, respectively. However, the presence of soot had certain effects on the NO_x profiles, as will be discussed next.

The nature of the dopant, M, strongly affected the NO_x chemisorption-release processes (Figure 1b). It was concluded from previous temperature programmed experiments carried out using CuO/Ce_{0.8}M_{0.2}O₈ catalysts without soot [23] that the acid/basic character of the dopants plays a major role in the interaction of NO_x with the catalyst support. A correlation was found between the acid/basic character of M and the threshold temperature above which NO_x release took place, following the trend:



Some consistencies with this trend are observed in Figure 1b, but the relationship between acid/basic character of M and the NO_x chemisorption/release was not completely fulfilled. For instance, considering the behaviour of the CuO/CeO₂ catalyst (Figure 1b), Zr⁴⁺ doping led to a decrease of the NO_x chemisorption capacity, which occurred from 150 to 260°C (Figure 1b), and also to a decrease of the stability of the chemisorbed NO_x species that were released above 340°C. On the contrary, ceria doping

with basic cations such as La^{3+} , Pr^{3+} or Nd^{3+} improved the chemisorption of NO_x and enhanced the thermal stability of the stored species with regard to CuO/CeO_2 . However, the trends of the NO_x storage capacity of catalysts with La^{3+} , Pr^{3+} or Nd^{3+} and of the stability of the stored species deduced from Figure 1b ($\text{CuO}/\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_8 < \text{CuO}/\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_8 \approx \text{CuO}/\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_8$) do not match the trend of basicity of the doping cations ($\text{Nd}^{3+} < \text{Pr}^{3+} < \text{La}^{3+}$). These discrepancies must be attributed to the presence of soot. It is known that carbonaceous materials can react with NO_x contributing to NO_x reduction [34, 35], and it cannot be ruled out that the combustion of soot leads to a localised increase in temperature which enhances the rate of desorption of NO_x stored on the catalysts. Also, the chemisorption of CO_2 as a soot combustion product on the catalyst would compete with NO_x for storage sites, and it cannot be ruled out that this competition affected the stability of the chemisorbed NO_x . The effect of the presence of soot in the NO_x removal process is also better studied in the isothermal experiments discussed in the next section.

The nature of the nitrogen species stored on the catalysts during the temperature programmed experiments was monitored by DRIFT spectroscopy. The region $1700\text{-}1000\text{ cm}^{-1}$ is shown (Figure 2) where the most relevant bands due to nitrogen- and carbon-containing species appear. Poly and mono-dentate carbonates usually show bands due to the antisymmetric and symmetric stretching modes of the terminal CO bonds around 1480 and 1350 cm^{-1} , respectively [36]. A certain decrease was observed at these wavenumbers (Figure 2), because carbonates were progressively replaced by chemisorbed NO_x . However, when spectra obtained with soot-catalyst mixtures (Figure 2) are compared with those obtained in similar experiments performed without soot (Figure 2 in Ref [23]), which were previously discussed in detail elsewhere [23], it can be concluded that the extent of depletion of carbonates in experiments without soot was higher than that

occurring in the presence of soot. This suggests that part of the CO₂ produced as a soot combustion product becomes chemisorbed on the catalysts.

Before discussing in detail, the behaviour of the different species as indicated by bands due to nitrogen species observed in Figure 2 it is worth mentioning that has been recently reported that the molar absorption coefficients of the overlapping bands of carbonates and nitrates are not identical. For this reason, the true position of the nitrate and nitrite bands cannot be assessed within such complex spectra [37, 38]. However, despite this limitation of the system under study, some conclusions can be reached by bearing in mind that the position of the nitrite and nitrate bands indicated in the following discussion may differ from those described for other carbonate-free systems.

Bands attributed to nitrogen-containing species grow with temperature in Figure 2. A band at 1200-1180 cm⁻¹ assigned to bridging nitrites ((M-O)₂=N) [39] grew for all catalysts at 150-200°C, which are probably formed upon NO chemisorption on the catalyst support. At 200°C a band appeared at 1435 cm⁻¹ that can be assigned to nitro groups (M-NO₂) [39], which remained stable until the maximum temperature of the experiments (500°C), and nitrate bands were identified in spectra recorded at 250°C and above. The main nitrate bands appeared around 1545, 1235 and 1010 cm⁻¹ and these frequencies are consistent with the presence of monodentate (M-O-NO₂) or bidentate (M-O₂NO) nitrates [39]. Nitrates can be formed either indirectly by oxidation of nitrogen species already chemisorbed on the catalysts, such as nitrites, or by direct chemisorption of NO₂. Spectra indicate that the nature of the nitrogen species present depends on the oxidation capacity of the catalysts, which increases with temperature following the trend: 150°C ⇒ nitrites (N (III)) ⇒ nitro (N (IV)) ⇒ nitrates (N (V)) ⇒ 500°C

In conclusion, these temperature programmed experiments provide evidence that the simultaneous chemisorption of NO_x and combustion of soot can take place above 375°C with the CuO/Ce_{0.8}Mo_{0.2}O₈ catalysts. Above this temperature, NO_x species were mainly stored in the form of nitrates, indicating that the oxidation capacity of the catalysts was sufficiently high to oxidise N (II) (in NO) to N (V). Also, evidence regarding the consequence of soot combustion on the NO_x storage process were observed. The combustion of soot affected the thermal stability of the NO_x species chemisorbed on the catalysts, and several hypothesis could be postulated to explain this: the local increase of temperature due to the exothermic combustion of soot destabilises the stored species, soot reacts with the chemisorbed NO_x species and/or the CO₂ yielded as a combustion product of soot competes with NO_x for chemisorption sites on the catalysts.

3.2. Isothermal experiments at 400°C without H₂ pulses.

Isothermal experiments were carried out at 400°C with soot-catalyst mixtures. This temperature was selected on the basis of results of the previous temperature programmed experiments, where it was observed that the onset temperature for the catalytic combustion of soot with CuO/Ce_{0.8}Mo_{0.2}O₈ was 375°C. However, the soot combustion rate measured under isothermal conditions at 375°C was too slow to properly screen catalysts performance, and for this reason it was increased to 400°C. It is important to note that the uncatalyzed reaction did not take place at a measurable rate at this temperature. It was also previously demonstrated [23] that the elimination of NO_x with the CuO/Ce_{0.8}Mo_{0.2}O₈ catalysts could be achieved at 400°C using NSR procedures and therefore, this temperature is appropriate to study the simultaneous removal of NO_x and soot.

The m/z 44 signal was used to monitor the release of CO_2 for the isothermal experiments carried out at 400°C with soot-catalyst mixtures, and from this release the conversion of soot was calculated. The isothermal experiments were conducted until total conversion of soot, that is, until the m/z 44 signal reached the baseline level. In all isothermal experiments where total conversion of soot was attained, the mass balance of carbon was properly closed with an error below 5% in all cases, and this indicated that the potential release of CO as a soot combustion product and subsequent accumulation of CO_2 on the catalysts had a marginal contribution to the estimation of soot conversion using the m/z 44 profile.

The soot conversion profiles obtained in experiments performed without H_2 pulses are compiled in Figure 3. The most active catalyst of those studied was CuO/CeO_2 , and all M dopants led to a delay in the soot conversion profiles. This observation is consistent with results reported for different ceria-based soot combustion catalysts [32, 40]. It is known that dopants improve the thermal stability of ceria and enhance the mobility of oxygen within the ceria lattice, and these benefits are very relevant for ceria catalysts thermal-treated at high temperatures (roughly above $600\text{--}700^\circ\text{C}$). However, for ceria catalysts calcined at lower temperatures (500°C in this study) the presence of dopants have zero or negative effect in mild-temperature soot combustion because they have a diluting effect. That is, there are less cerium cations per unit mass of catalyst and the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple responsible for the high soot combustion catalytic activity of these materials is negatively affected.

The removal of NO_x during the catalytic combustion of soot at 400°C was evaluated, and the profiles obtained are included in Figure 4. The NO_x removal profiles obtained in similar experiments performed with only the catalysts (without soot) are also

included for comparison. This comparison is useful in order to identify the different NO_x removal pathways and the weight of each to the total removal.

All CuO/Ce_{0.8}M_{0.2}O₈ catalysts chemisorbed NO_x from the gas stream, as deduced from the NO_x removal profiles (Figure 4) of experiments performed without soot, and the NO_x removal levels dropped to zero once the catalyst was saturated. NO_x chemisorption on the catalysts also took place in isothermal experiments performed with soot-catalyst mixtures. However, the presence of soot strongly affected this chemisorption in some cases, and the nature of the M dopant played an important role. For instance, the NO_x removal profiles obtained with CuO/Ce_{0.8}Zr_{0.2}O₈ (Figure 4a) in experiments with and without soot were similar during 25 minutes, and after this time, the removal of NO_x was higher in the experiment performed with soot. This indicated that the soot-NO_x reaction contributed to NO_x removal. In the case of the CuO/Ce_{0.8}Zr_{0.2}O₈ catalyst, the NO_x-soot reaction only contributed to NO_x removal when the catalyst reached a certain level of saturation and continued until total consumption of soot. This suggests that NO_x chemisorption occurs preferably to the soot-NO_x reaction.

The NO_x removal behaviour of the CuO/CeO₂ catalyst (Figure 4b) was qualitatively similar to that described for CuO/Ce_{0.8}Zr_{0.2}O₈ (Figure 4a; note that Zr⁴⁺ is the most acidic dopant among those studied), but it changed for catalysts doped with basic cations (M = Nd, Pr and La; Figures 4c, 4d and 4e, respectively). For instance, the removal of NO_x by the catalyst with the most basic cation (CuO/Ce_{0.8}La_{0.2}O₈; Figure 4e) drops significantly in the presence of soot, and the effect of soot on the removal of NO_x over CuO/Ce_{0.8}Nd_{0.2}O₈ (Figure 4c) and CuO/Ce_{0.8}Pr_{0.2}O₈ (Figure 4d) lies between those described for the catalysts with the most acidic (Zr⁴⁺) and most basic (La³⁺) cations.

The amounts of NO_x removed from the gas stream under isothermal conditions at 400°C in the presence and absence of soot were quantified and compiled (Table 1). As it has been already indicated, the removal of NO_x in experiments performed without soot must be only attributed to NO_x chemisorption on the catalysts while the reduction of NO_x by soot additionally contributed to NO_x removal in experiments performed with soot-catalyst mixtures. As previously discussed [23], the amounts of NO_x chemisorbed on the catalysts in the absence of soot increased with the basic character of the M dopant. Note that, in Table 1, the basicity increases from top to bottom (most acidic \Rightarrow Zr⁴⁺ < none < Nd³⁺ < Pr³⁺ < La³⁺ \Leftarrow most basic). On the other hand, the removal of NO_x in experiments performed with soot did not follow the trend with respect to M basicity. The greatest removal of NO_x was achieved with CuO/CeO₂ (421 μ molNO_x/g_{catalyst}), followed by CuO/Ce_{0.8}Pr_{0.2}O₈ (389 μ molNO_x/g_{catalyst}), and the poorest being CuO/Ce_{0.8}La_{0.2}O₈ (176 μ molNO_x/g_{catalyst}).

It is interesting to analyze the differences between the amounts of NO_x removed in experiments performed with and without soot, and these values are also included in Table 1. The effect of soot on the removal of NO_x was most detrimental for the catalyst with the most basic dopant (CuO/Ce_{0.8}La_{0.2}O₈; -190 μ molNO_x/g_{catalyst}), that is, the presence of soot hinders the chemisorption of NO_x on CuO/Ce_{0.8}La_{0.2}O₈ and the contribution of the soot-NO_x reaction to NO_x removal was low, the net balance being clearly negative. The same conclusion was obtained by other authors that also studied the chemisorption of NO_x in the presence of soot on catalysts with very basic adsorbents, such as Pt-Ba/Al₂O₃ [19, 20]. On the other hand, for the other two catalysts with basic dopants (CuO/Ce_{0.8}Nd_{0.2}O₈ and CuO/Ce_{0.8}Pr_{0.2}O₈) the negative effect of soot on the chemisorption of NO_x was compensated by the removal of NO_x by reduction with soot,

and the net balances were close to zero (30 and 21 $\mu\text{molNOx/g}_{\text{catalyst}}$). The presence of soot was clearly positive in terms of NOx removal using catalysts without dopant (CuO/CeO_2) or with an acidic dopant ($\text{CuO/Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$), confirming that the soot-NOx reaction contributed to NOx removal without significantly impacting on the chemisorption of NOx. These results and others [19, 20, 21] lead us to believe that the negative effect of soot on NOx storage is only prevalent for catalysts with very basic character, and therefore, the acid/basic properties of the catalyst must be optimized to avoid the negative effect of soot but also to maximize NOx removal as much as possible. Ceria cation doping seems to be an appropriate approach for this purpose.

Different hypotheses have been proposed to explain the negative effect of soot on NOx storage on Pt-Ba/ Al_2O_3 catalysts. It has been proposed that the combustion of soot ages the catalysts by causing Pt sintering and Ba agglomeration [21]. However this hypothesis is inconsistent with the fact that the negative effect of soot on NOx removal disappears when H_2 is fed to reduce the stored NOx species [41]. Some authors have proposed that the negative effect of soot on NOx storage on Pt-Ba/ Al_2O_3 is due to the chemisorption of the CO_2 produced as a product of soot combustion product [42] and others suggest that the presence of carbon destabilizes the chemisorbed NOx species [19]. In our opinion, these two interpretations could contribute and may be related to each other. That is, the destabilization of the chemisorbed NOx species could be due to the chemisorption of CO_2 emitted upon soot combustion, but other destabilization mechanisms could be also feasible and, with the experimental evidence available, it is not possible to confirm which is the main contributing factor.

The DRIFT spectra recorded under operando conditions isothermally at 400°C with soot- $\text{CuO/Ce}_{0.8}\text{M}_{0.2}\text{O}_8$ mixtures provide valuable information regarding

chemisorption of NO_x on the catalysts and about the influence of soot combustion in this process. These DRIFT spectra are shown in Figure 5 for all catalysts.

The main bands that grow with time around 1550 and 1230 cm⁻¹ can be assigned to nitrates [39], in agreement with the conclusions of the temperature programmed experiments. Nitrates of different configuration were formed on CuO/Ce_{0.8}Zr_{0.2}O₈ (Figure 1a) and CuO/CeO₂ (Figure 1b) catalysts, as deduced for instance, from the maxima at ~1600, ~1550 and ~1530 cm⁻¹ that would be consistent with the formation of bridging, bidentate and monodentate nitrates, respectively. On the contrary, the position of the nitrate bands for catalysts with Nd, Pr or La are consistent with the formation bidentate nitrates. The formation of nitro groups is also inferred from the bands at 1400 cm⁻¹ [39], and these species seem to remain stable during the whole experiment for CuO/Ce_{0.8}Zr_{0.2}O₈ and CuO/CeO₂ but not in the case of Nd, Pr or La.

In addition to nitrogen species, a shoulder is observed at 1485 cm⁻¹ in the spectra (Figure 5e) of the catalyst containing the most basic dopant (CuO/Ce_{0.8}La_{0.2}O₈) that could be assigned to carbonates. This would support the hypothesis that the chemisorption of the CO₂ produced by soot combustion competes with the chemisorption of NO_x and would explain why the CuO/Ce_{0.8}La_{0.2}O₈ catalyst chemisorbs much more NO_x in the absence than in the presence of soot (Figure 4e and Table 1). This band at 1485 cm⁻¹ due to carbonates was not so obvious in the spectra of the other catalysts, although a certain level of carbonation cannot be ruled out as discussed elsewhere [43]. The differences in terms of the 1485 cm⁻¹ band intensity would be consistent with the fact that catalysts with basic dopants are more prone to suffer the negative effects of soot on NO_x chemisorption due to the CO₂ emitted as a soot combustion product.

3.3. Isothermal experiments at 400°C with H₂ pulses.

An isothermal soot combustion experiment was performed at 400°C with CuO/Ce_{0.8}Pr_{0.2}O₈ and H₂ pulses, and the results are shown in Figure 6 together with those of a similar experiment performed without H₂. CuO/Ce_{0.8}Pr_{0.2}O₈ was the most active catalyst for NO_x chemisorption (Table 1) and soot combustion (Figure 3) after CuO/CeO₂. However, it is very well known that neat ceria is prone to deactivate under real operating conditions due to sintering, and so doping with other cations is essential to attain suitable thermal stability [40]. For this reason, CuO/Ce_{0.8}Pr_{0.2}O₈ was selected for this NSR experiment.

Figure 6a presents the soot conversion profiles with and without H₂ pulses and Figure 6b the corresponding NO_x concentrations (m/z 30 signals). These results demonstrate that soot (Figure 6a) and NO_x (Figure 6b) can be simultaneously removed following the NSR approach (see curves obtained with H₂ pulses). As it is shown in the inset of Figure 6b, the NO_x profile obtained in the experiment with H₂ pulses follows the shape of the pulses because. Once H₂ was introduced, most of the NO_x stored on the catalyst was reduced yielding N₂ and a small fraction was released without undergoing reduction. The release of N₂ as NO_x reduction product is deduced from the shape of the m/z 28 signal, which also follows the shape of the pulses. The high selectivity of the Copper/Ceria NSR catalysts towards N₂ formation was also observed in the previous articles of this series [22,23]. It is worth noting that the potential release of CO as soot combustion product could contribute to the m/z 28 signal, and this would affect the interpretation of the m/z 28 profile and the assignation to N₂. However, the formation of CO as soot combustion product is not expected. CO was not observed during the

experiment performed without H₂ pulses and is neither expected to be released in the experiments with H₂.

NO_x removal by the NSR method had a positive effect on the catalytic combustion of soot. Soot oxidation took place faster when H₂ was pulsed (compare curves in Figure 6a), and two arguments can be postulated to explain this observation: (i) the destabilization of the stored nitrates upon H₂ pulses leads to the formation of high local concentrations of NO₂ that contribute to soot combustion because NO₂ is highly oxidizing and/or (ii) the oxidation of H₂ leads to the localised increase in temperature, which enhances soot combustion.

The nature of the species chemisorbed on the catalyst during these isothermal soot combustion experiments was monitored by rapid-scan DRIFTS, and only nitrates were detected. The band at 1550 cm⁻¹ due to nitrates was selected to monitor changes in their population during the isothermal experiments, and the absorbance at this wavenumber as a function of time is plotted in Figure 7. The nitrate band intensity monitored during the experiment performed without H₂ pulses shows fluctuations only arising from signal noise. In contrast, the absorbance at 1550 cm⁻¹ monitored during H₂ pulses followed the shape of the pulses, in accordance with the results obtained in NSR experiments performed with the CuO/Ce_{0.8}Mo_{0.2}O₈ catalysts (without soot) discussed in a previous article [23]. This shape is produced because the H₂ pulse partially regenerates the catalyst, which is again saturated with NO_x between consecutive pulses. Note that the peaks of the profile of absorbance at 1550 cm⁻¹ in the experiments with H₂ pulses were much better defined when soot was almost consumed (Figure 7b; 95-98 % soot burn off) than when soot was still available in quantity and thus undergoing significant reaction (Figure 1a; 11-22% burn off). This could indicate that the depletion of surface nitrates during the

combustion of soot under NSR conditions not only occurs due to the H₂ pulses but also due to reaction with soot.

In conclusion, it is demonstrated that the simultaneous removal of NO_x and soot can be carried out under NSR conditions at 400 °C with a 5% Cu/Ce_{0.8}Pr_{0.2}O₈ catalyst, and the NSR process has a positive effect on soot combustion.

4.- Conclusions.

Copper catalysts with Ce_{0.8}M_{0.2}O₈ supports (M = Zr, La, Ce, Pr or Nd) were studied for the simultaneous combustion of soot and removal of NO_x by the NSR method, and the following conclusions can be drawn:

- The simultaneous chemisorption of NO_x and combustion of soot can be carried out above 375°C. Above this temperature the main NO_x species stored on the catalysts were nitrates in different configurations, providing evidence that the oxidation capacity of the catalysts was sufficiently high to oxidise N (II) (in NO) to N (V) (nitrates).
- The presence of soot affects the chemisorption of NO_x on the catalysts, and the nature of the M dopant plays an important role in the chemisorption of NO_x and in the catalysed soot-NO_x reaction. As a general trend, the presence of soot is negative for NO_x removal by catalysts with very basic supports while is null or positive if the support is not very basic.

- The combustion of soot has a detrimental effect on NO_x chemisorption on the catalyst with the most basic dopant (CuO/Ce_{0.8}La_{0.2}O₈), because the chemisorption of CO₂ emitted as a soot combustion product competes with NO_x for the adsorption sites.
- In contrast, soot combustion does not affect NO_x chemisorption on the catalyst with the most acidic dopant (CuO/Ce_{0.8}Zr_{0.2}O₈), and the removal of NO_x increases in this case because the reduction NO_x by soot also removes NO_x.
- The simultaneous removal of NO_x and soot can be carried out under NSR conditions at 400°C with the 5% Cu/Ce_{0.8}Pr_{0.2}O₈ catalyst and with H₂ micropulses, and the NSR process improves the catalytic combustion of soot.

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Figure captions

Figure 1. Temperature programmed experiments performed with 1:20 loose contact soot-catalyst mixtures (otherwise indicated). (a) CO₂ release, (b) NO_x concentration and (c) NO₂ percentage with regard to total NO + NO₂.

Figure 2. DRIFT spectra monitored during temperature programmed experiments performed with 1:20 loose contact soot-catalyst mixtures. (a) CuO/Ce_{0.8}Zr_{0.2}O₈, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O₈, (d) CuO/Ce_{0.8}Pr_{0.2}O₈ and (e) CuO/Ce_{0.8}La_{0.2}O₈.

Figure 3. Soot conversion in isothermal experiments performed at 400°C with 1:20 loose contact soot-catalyst mixtures (without H₂ pulses). Uncatalysed soot combustion did not take place in these conditions.

Figure 4. NO_x removal in isothermal experiments performed at 400°C with CuO/Ce_{0.8}M_{0.2}O₈ catalysts and with 1:20 loose contact soot-catalyst mixtures (without H₂ pulses). (a) CuO/Ce_{0.8}Zr_{0.2}O₈, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O₈, (d) CuO/Ce_{0.8}Pr_{0.2}O₈ and (e) CuO/Ce_{0.8}La_{0.2}O₈.

Figure 5. DRIFT spectra monitored as a function of time during isothermal experiments performed at 400°C with 1:20 loose contact soot-catalyst mixtures (without H₂ pulses). (a) CuO/Ce_{0.8}Zr_{0.2}O₈, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O₈, (d) CuO/Ce_{0.8}Pr_{0.2}O₈ and (e) CuO/Ce_{0.8}La_{0.2}O₈.

Figure 6. Isothermal experiments performed at 400°C with 1:20 loose contact soot-CuO/Ce_{0.8}Pr_{0.2}O₈ mixtures with and without H₂ pulses. (a) Soot conversion and (b) NO_x concentration.

Figure 7. Absorbance at 1550 cm⁻¹ (nitrates) monitored by rapid-scan DRIFTS during isothermal experiments performed at 400°C with 1:20 loose contact soot-CuO/Ce_{0.8}Pr_{0.2}O₈ mixtures with and without H₂ pulses. (a) minutes 20 to 30 (b) minutes 165 to 175.

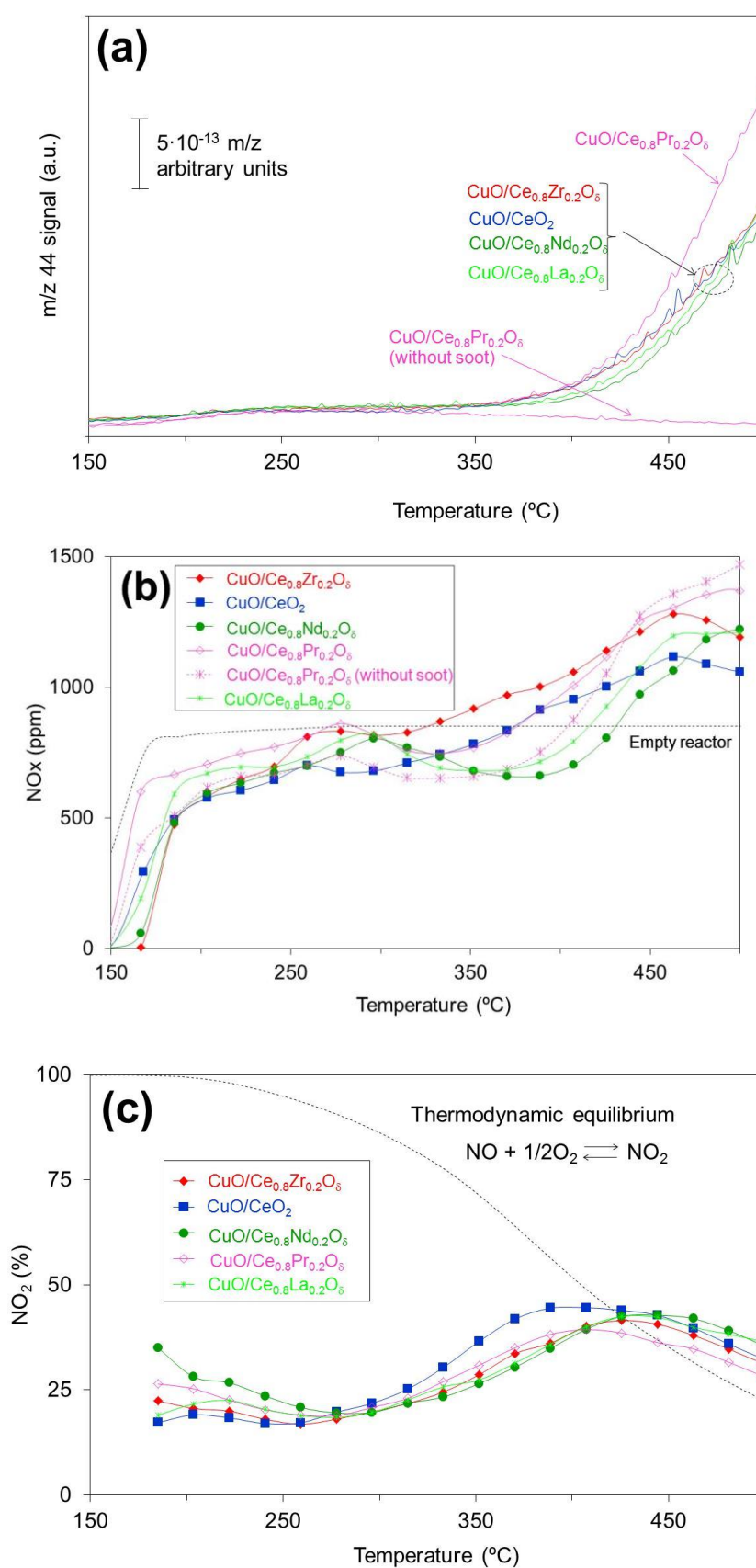
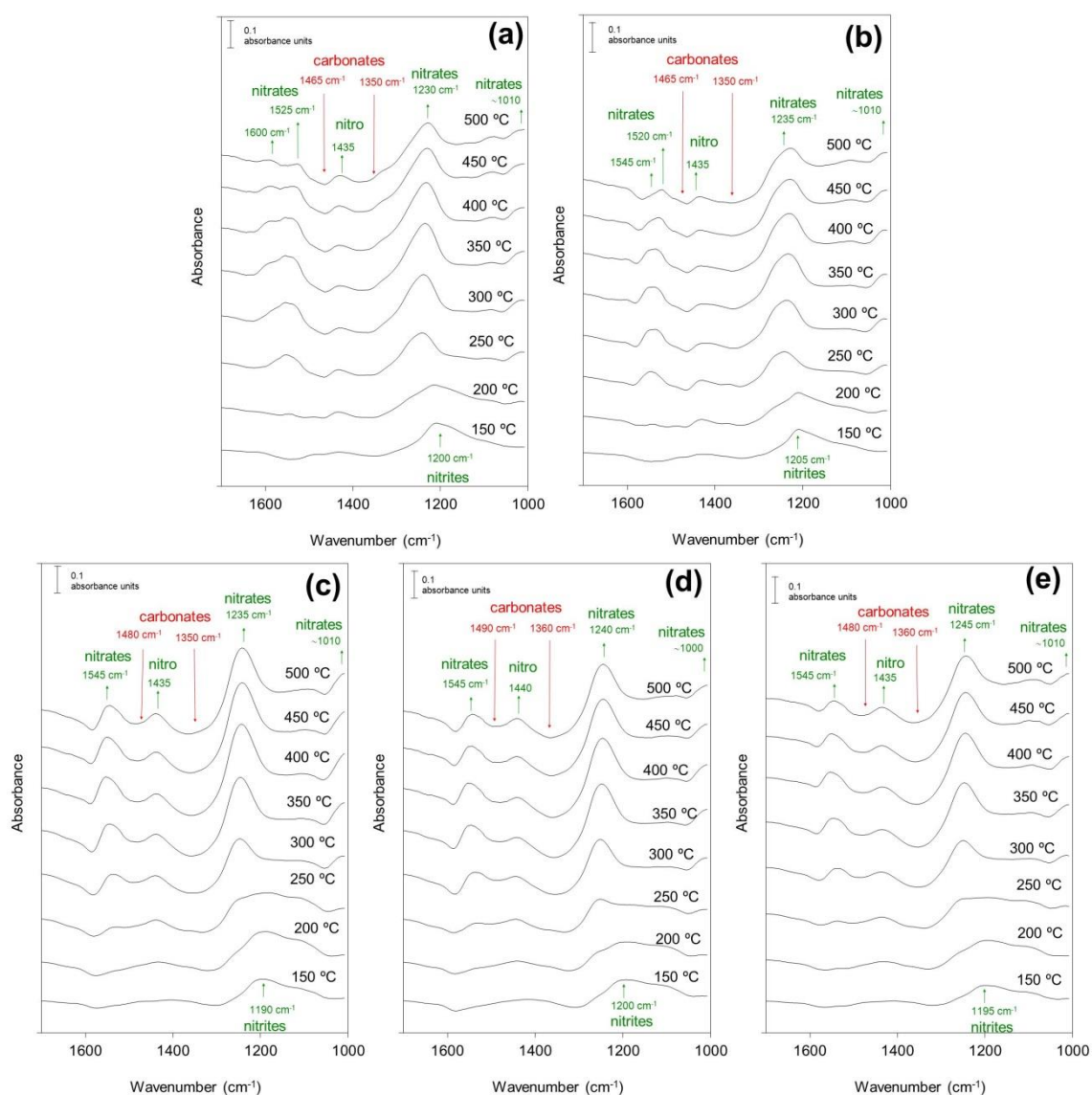
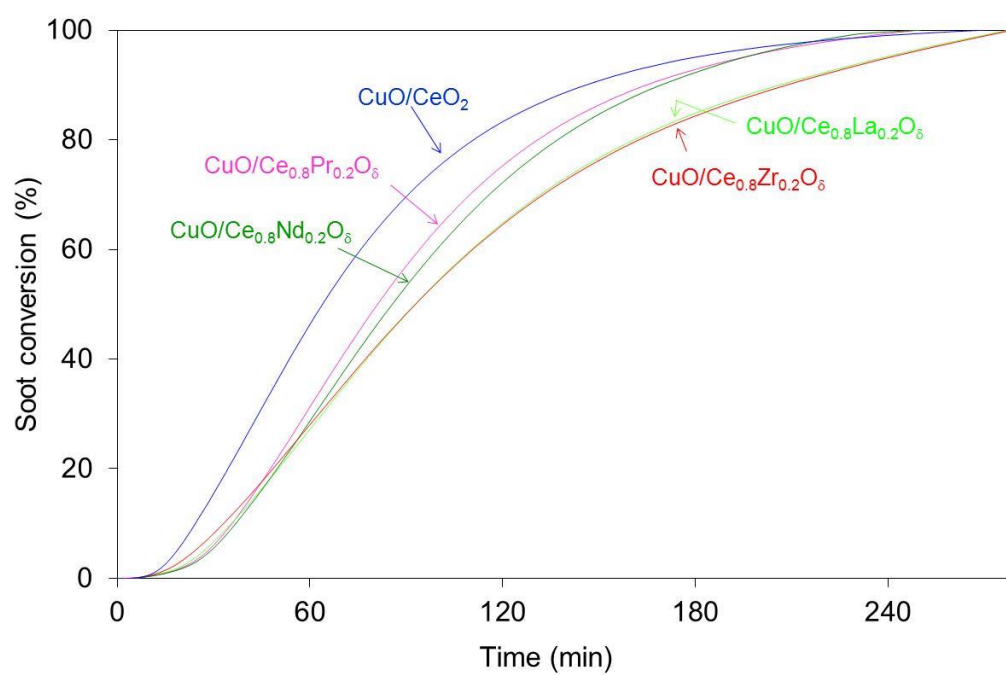
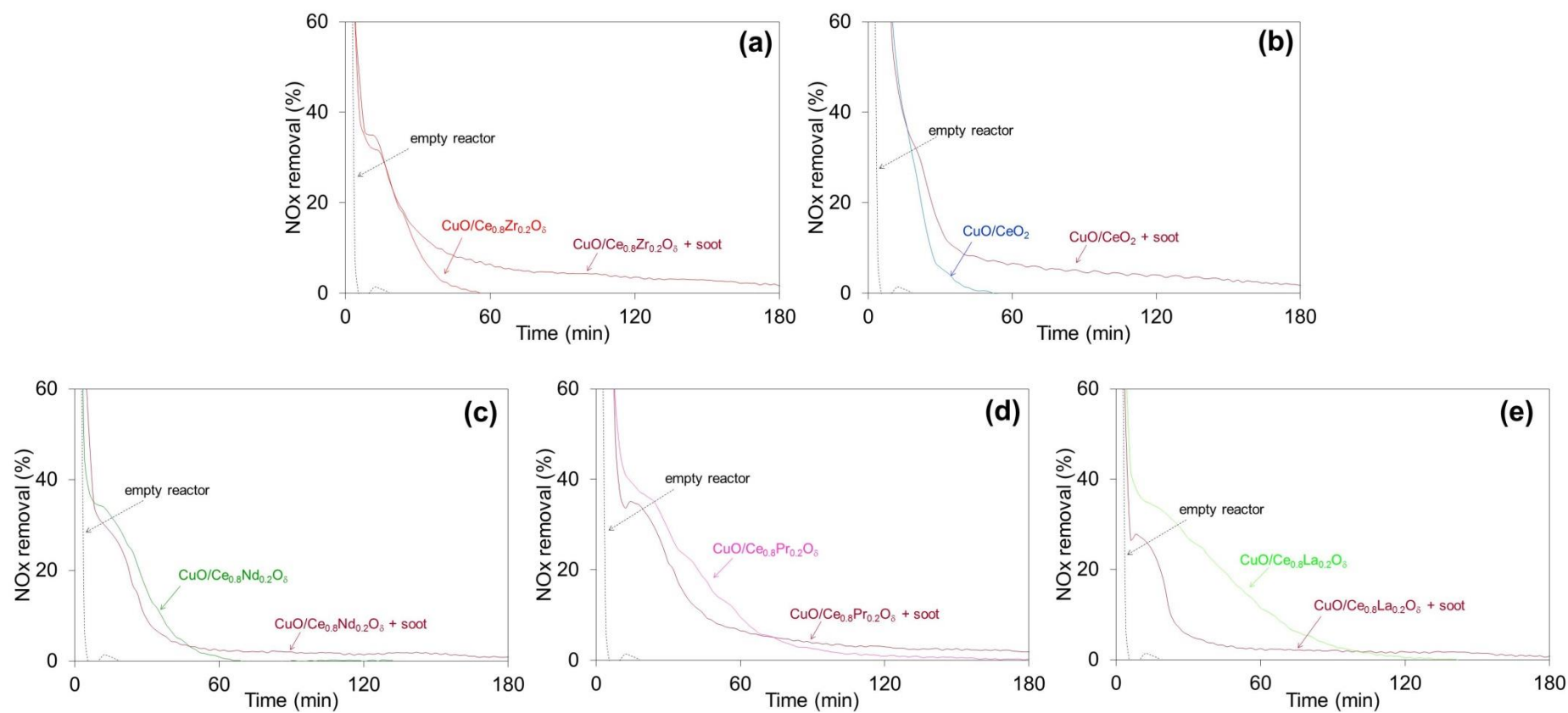
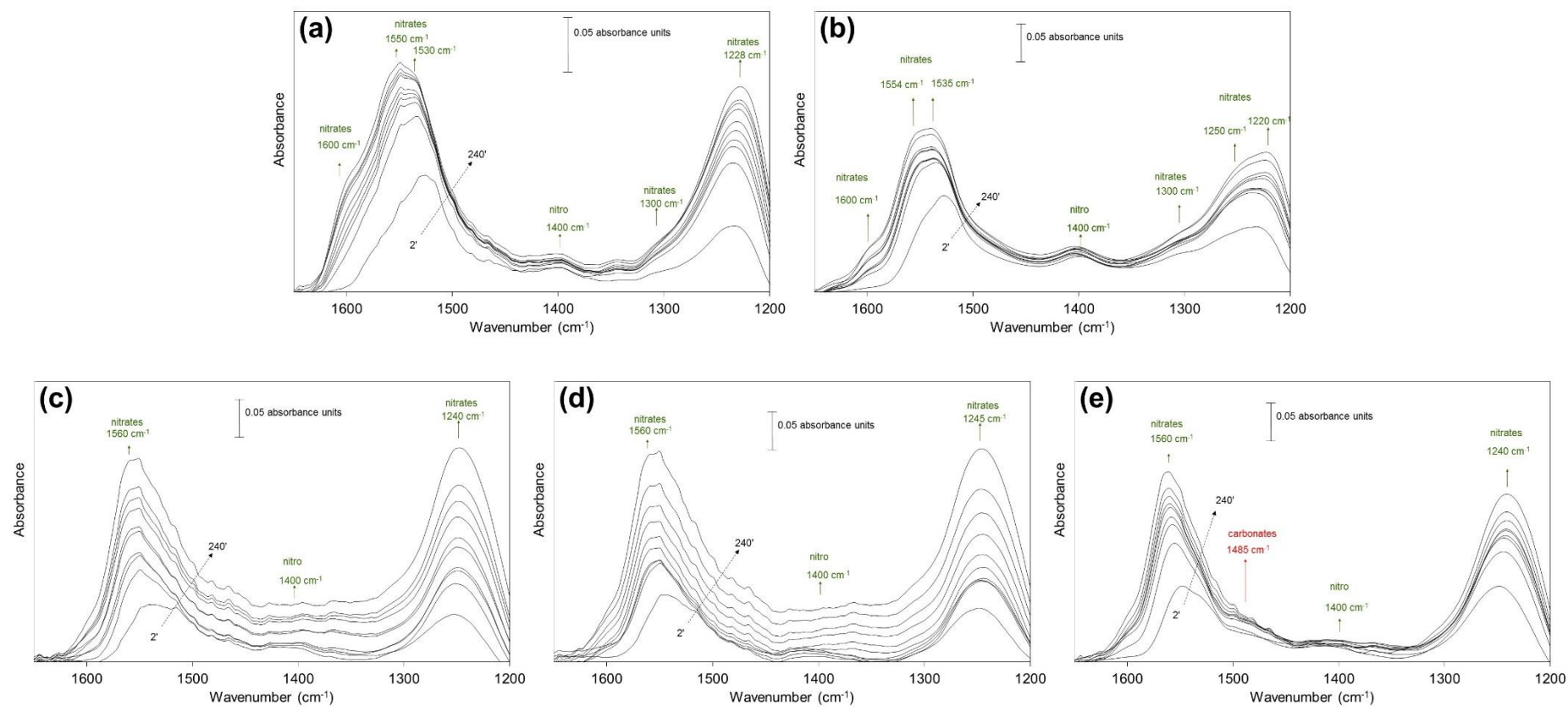


FIGURE 1

**FIGURE 2**

**FIGURE 3**

**FIGURE 4**

**FIGURE 5**

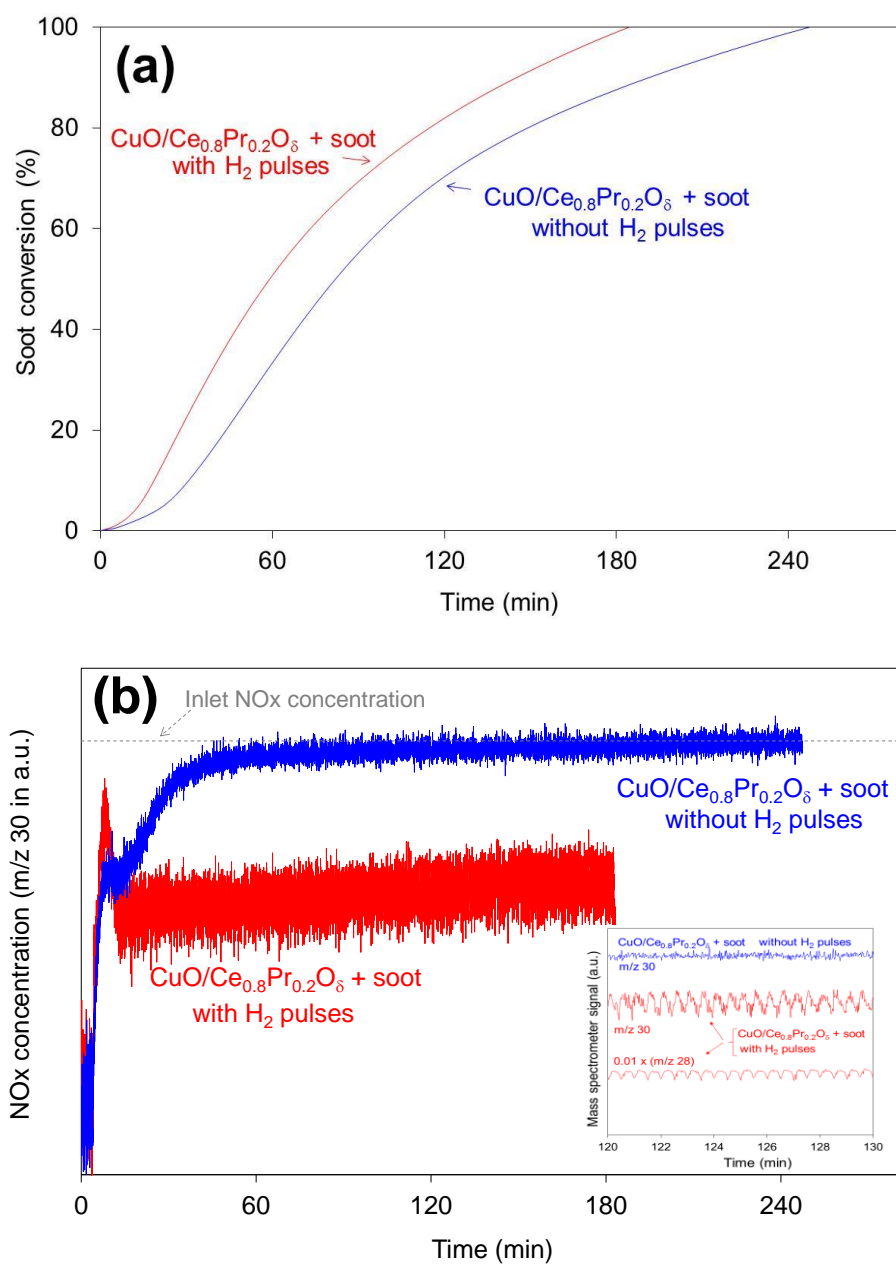


FIGURE 6

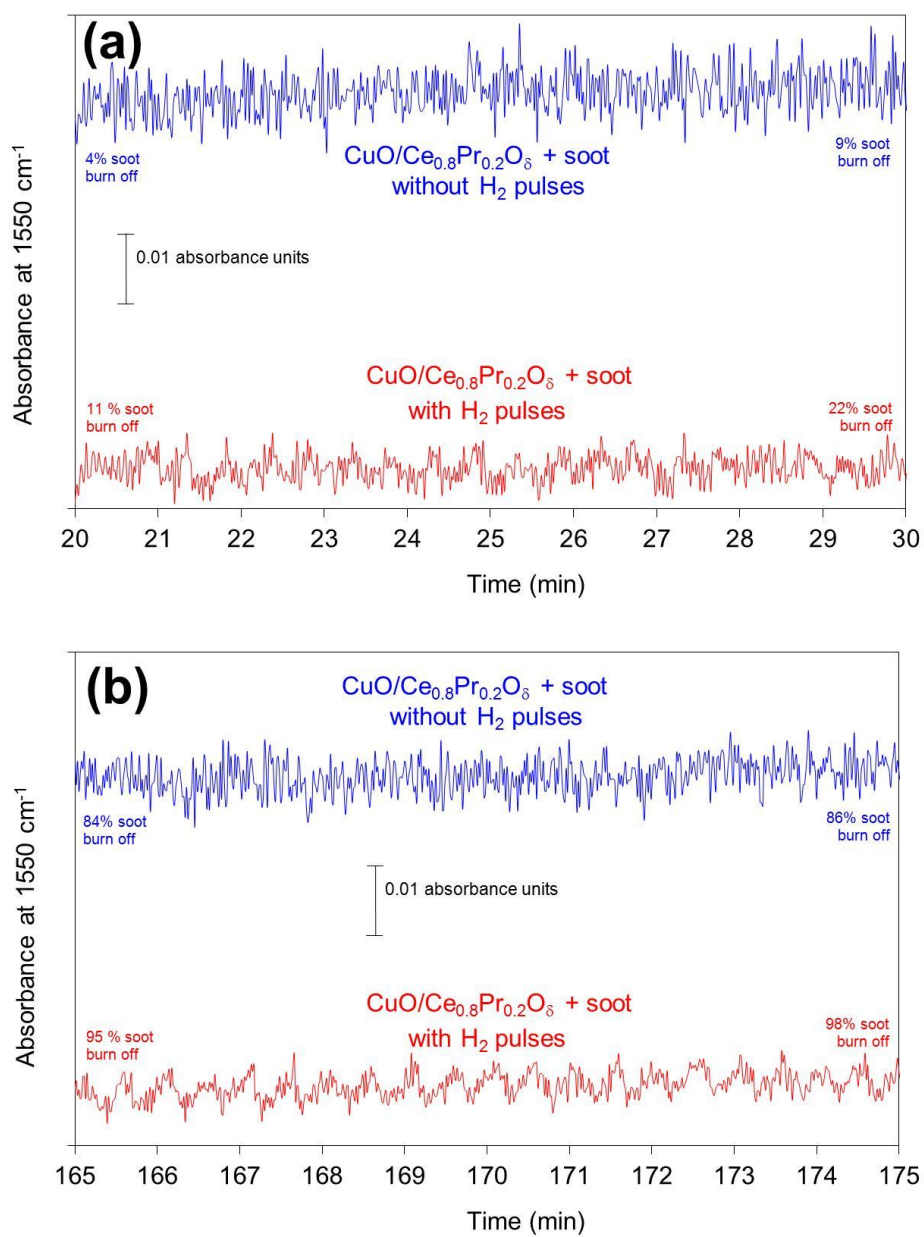
**FIGURE 7**

Table 1. Amount of NO_x removed from the gas stream at 400°C (in $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$) in experiments without and with soot.

| Catalyst | Without soot ^a | With soot ^b | With soot – Without soot |
|--------------------------------------------------------|---------------------------|------------------------|--------------------------|
| CuO/Ce _{0.8} Zr _{0.2} O ₈ | 166 | 320 | 154 |
| CuO/CeO ₂ | 168 | 421 | 253 |
| CuO/Ce _{0.8} Nd _{0.2} O ₈ | 198 | 228 | 30 |
| CuO/Ce _{0.8} Pr _{0.2} O ₈ | 368 | 389 | 21 |
| CuO/Ce _{0.8} La _{0.2} O ₈ | 366 | 176 | -190 |

^aNO_x are chemisorbed on the catalyst.

^bNO_x are chemisorbed on the catalyst and reduced by soot.